AN INTRODUCTION TO ULTRAVIOLET LIGHT (UV) AND ELECTRON BEAM (EB) CURABLE COATING TECHNOLOGY

BACKGROUND

Ultraviolet light (UV) and electron beam (EB) curable materials are unique solvent-free compositions that cure (harden) in a fraction of a second upon exposure to a UV or EB source. The absence of solvent eliminates the need for large baking ovens used to process conventional solvent-based coatings and inks. Industry's interest in UV/EB curable coating technology began in the 1960s. For example, the beverage industry's interest in UV/EB curable coatings was sparked by the government's announced program to begin allocating natural gas. Beverage companies were dependent on natural gas to process conventional solvent-based inks and coatings used to decorate beverage cans. The commercialization of UV curable inks in the 1970s enabled beverage companies to accommodate a reduced availability of natural gas with a technology that depended solely on readily available electric energy. As a bonus, companies such as Coors found that switching to UV curable inks for metal can decoration substantially reduced energy and operational costs. These savings amounted to more than one million dollars per year.[1]

The use of UV/EB curable materials spread to other parts of the printing industry, based on the exceptional performance properties this technology offers as compared to conventional coatings. The in-line application of UV curable clear coatings in a conventional four-color printing process eliminates the need for spray powder. Spray powder was typically used to prevent the wet ink from offsetting while the printed stock is stacked waiting to be fabricated. By replacing spray powder with a UV curable coating on the last station of the printing press, the coated stock can be immediately fabricated as it comes off the press. The use of UV coatings significantly increases productivity by eliminating the need to wait for the conventional ink to dry. Printers using UV/EB curable inks for general printing achieve additional advances in productivity and process versatility.

Optical fiber manufacturers found UV curable coatings to be the only coating technology that would satisfy the fast line speeds needed to make optical fibers a commercial reality. Today, optical fibers are being drawn at speeds greater than 5,000 feet/minute using UV curable coatings. The printing and optical fiber industries are just two examples illustrating why UV/EB curable coatings are chosen over other coating technology for performance advantages. Additional uses of UV/EB curable coating technology will be discussed later in this paper.

Today's manufacturing environment, in which government is imposing strict reductions in emission of volatile organic compounds (VOC) and hazardous air pollutants (HAP), offers another strong incentive for industry to switch to UV/EB curable coating technology.

BENEFITS OF USING UV/EB CURABLE COATINGS

In addition to the already mentioned fast line speed (higher productivity) and solvent-free compositions, UV/EB curable coatings offer many more important benefits. These include:

- Reduced floor space – UV/EB curing equipment is much more compact than conventional drying ovens, and the solvent-free compositions require less storage space than solvent-based coatings providing comparable dry film weight.
- Suitable for heat-sensitive substrates – The fast line speeds achieved with UV/EB curable coatings and absence of thermal drying result in a relatively cool coating process which can be used for coating heat sensitive substrates, such as plastic, wood and paper.
- Reduced in-process inventory – A conventional thermal curing coating manufacturing process, requiring intermediate drying stages, can be converted into a single-step, in-line process with UV/EB curable coatings.
- Lower insurance costs and reduced handling hazards – Solventless UV/EB curable coatings are rated as non-flammable liquids. This will result in reduced insurance costs, less stringent storage requirements and a reduction in handling hazards compared to flammable solvent-based coatings.
- Compliant technology – Federal, state and local governments recognize the many advantages offered by UV/EB curable coatings in complying with VOC and HAP restrictions.[2, 3, 4] For example, UV curable coatings for metal can application has been reported by the EPA to contain

less than 0.01 VOC/gallon of coating.[5] Coors reported no significant emission of ozone or other undesirable emissions from a UV can line for one billion cans per year.[6]

- Reduced costs – Several studies show a significant reduction in energy costs can be achieved by switching from conventional thermal curing coatings to UV/EB curable coatings. Additional studies show that switching to UV/EB curable coatings is less expensive than converting an existing solvent- based coating operation into a VOC and HAP compliant operation.[7, 8]
- Proven technology – UV/EB curable coatings are a proven technology, used worldwide, that has been in commercial use since the 1960s.

THE CHEMISTRY OF UV CURABLE COATINGS

Most commercially used UV curable coatings are based on acrylate chemistry that cures via free radical polymerization. These liquid compositions typically contain a mixture of a reactive oligomer (30 – 60%), one or more reactive monomers (20 – 40%), a UV light-absorbing component (3 – 5%), and one or more additives (<1%). UV/EB curable inks may contain up to 20% pigment. A high pigment content such as used in UV inks typically requires up to 10% of photoinitiator

One of the many advantages of acrylate-based coatings is the extensive number of oligomers containing urethane groups that can be prepared to meet a wide range of cured film properties. Polyols used to prepare urethane acrylates for UV/EB compositions include polyethers, polyesters. Polybutadienes, etc.

Generally, a mixture of monofunctional (one acrylate group) and polyfunctional (more than one acrylate group) acrylates is used in order to optimize cured film properties and liquid coating cure speed. Monofunctional monomers tend to reduce viscosity more effectively than polyfunctional acrylates. The monofunctional monomers also reduce cured film shrinkage and increase the elasticity of the cured film. However, a high concentration of monofunctional monomer severely reduces the coating cure speed. Highly functionalized monomers increase coating cure speed and increase cured film resistance to abrasion. However, these two desirable cured film features are achieved at the sacrifice of embrittling the cured film and reducing adhesion to the substrate. Optimized coating properties are achieved by systematically selecting and balancing the ratio of oligomer and monomer concentrations.

The UV light absorbing component, called a photoinitiator, initiates the polymerization process upon exposing the liquid coating to an intense source of UV light. Photoinitiators typically absorb light in two wavelength regions: UV_A (260 nm) and UV_C (365 nm). The absorption at the higher energy (260 nm) is several orders of magnitude greater than the absorption at the lower energy (365 nm). The depth of UV light absorption for photoinitiators of known extinction coefficient can be calculated from the Beer-Lampert law written as follows:

$$\log P_0/P = A = Ecl$$

or

$$l = A/Ec$$

A = Measured absorbance of light
E = Extinction coefficient (liter/mole cm)
c = Concentration of absorbing solute (moles/liter)
l = Path length of medium which light travels (cm)
P = Power of light emerging from medium
P_0 = Power of incident light

Benzophenone absorbs UV light at 252 nm and 331 nm. The extinction coefficients are 18,000 and 156 respectively. As shown below, at 331 nm, 90% of a beam of UV light passing through a model coating containing 5% benzophenone will be completely absorbed at a depth of 234μm. At 252 nm, 90% of a beam of UV light passing through the same model coating will be completely absorbed at a depth of only 2 μm.

$$l\ (\mu m) = 1 \times \text{moles cm}/156 \text{ liter} \times \text{liter}/2.74\text{x}10^{-1}\text{moles} \times \mu m/1\text{x}10^{-4}\text{ cm} = 234\ \mu m$$

At 252nm (E = 18,900)

90% of the light will penetrate ~ 2 μm

A variety of photoinitiators are available that differ in wavelength absorption and mechanism for initiating polymerization. Wavelengths of intense absorption tend to favor coating surface cure while wavelength of lower absorption tends to favor coating through cure. Some applications require a combination of two or more different photoinitiators to achieve optimized cured film properties and coating cure speed.

The photoinitiator decomposes at a rate significantly faster than the rate of polymerization. It is this rapid photodecomposition that results in UV curable coating polymerizing instantaneously upon UV exposure.

Additives are a common ingredient typically used to optimize coating properties, such as liquid coating shelf life, cured film durability, adhesion to substrate and general cured film appearance.

The second most widely used UV curable composition is the cationic-cured coatings. Cationically-cured coatings are based on epoxy-polyol compounds that polymerize in the presence of an acid. The photoinitiator used in cationically-cured compositions generates a Bronsted acid upon exposure to UV light. One of the drawbacks in the cationically-cured systems is the limited raw material available for use in these formulations.

A comparison of the cationically-cured and free radical cured coating systems is shown in Table 1.

Feature	Cationic	Free-Radical
Cure speed	Moderate – fast	Fast
Post cure	Yes	No
Air inhibition (O_2)	No	Yes
Moisture sensitivity	Yes	No
Base sensitivity (high pH)	Yes	No
Urethane tolerant	No	Yes
Cured film shrinkage	Small	Moderate
Adhesion	Good – excellent	Moderate – excellent
Durability	Fair	High
Raw material availability	Limited	Extensive

Table 1

THE CHEMISTRY OF EB CURABLE COATINGS

Acrylate and epoxy-polyol compositions that cure with UV light can be cured by exposure to high-energy electrons commonly referred to as EB curing. The electrons used in the curing process range from 80 to as high as 300 Kv. The higher the voltage the deeper the electrons penetrate into the coated substrate. In the case of acrylates, no photoinitiator is required for EB curing. However, cationically-cured compositions require a small amount of acid producing photoinitiator. A comparison of UV versus EB curing is shown in Table 2. Table 3 shows UV light sources and Table 4 shows EB sources.

UV	EB
Requires a photoinitiator (higher cost)	No photoinitiator (except small amount for cationic compositions)
N_2 not always required	Requires N_2 for free radical compositions
Penetration decreases exponentially through coating thickness	Penetration more uniform: dependent on coating density
Penetration limited to UV transparent laminating materials	Penetration limited to density of laminating materials
No special license requirements	May require state license
Able to cure 3-D objects	Limited to 2-D objects

Table 2

UV LIGHT SOURCES

Feature	Electrode	Electrodeless	LED
Source	Mercury vapor	Mercury vapor	Light emitting diodes
Activated	Electrical	Microwave	Electrical
Response	Delayed on/off	Instant on/off	Instant on/off
Lamp length	Up to six feet	Ten inches	Can be scaled
Lamp lifetime	~1,000 hours	~2,000 hours	>10,000 hours
Use	General	General	inks and deep cure
Cooling	Air	Air	Water or air
Peak Irradiance	2 watts/cm^2	2 watts/cm^2	8 to 24 watts/cm^2
Spectral output	UVA, UVB, UVC	UVA, UVB, UVC	UVC

Table 3

EB Sources

FEATURE	SCANNING E BEAM[1]	CONTINUOUS E BEAM	CONTINUOUS COMPACT E BEAM
Voltage (Kv)	< 300	< 200	< 150
Depth of cure (1gr/cc)	14 mils	6 mils	3 mils
Shielding	Moderate – High	Minimum	Minimum
Current (ma)	<200	<1600	NA
Operating width (in)	80	120	10

1. Scanning EB sources can be as high as 1,000 Kv

Table 4

UV CURE REQUIREMENTS
Energy Density, sometimes referred to as dose, is expressed as Joules/cm^2 (1 Joule = 1 watt sec.). In general, UV curable coatings require a dose or radiant energy density of between 0.5 to 3.0 Joules/cm^2 to achieve full cure at reasonable line speeds. Additional cure may result in embrittlement and/or discoloration of the cured film. The energy density for a given process can be measured when 1, 2 and 3 below are well defined.

FOUR KEY PARAMETERS IN DEFINING THE UV CURING PROCESS

1. Irradiance (*intensity*)
Either peak or profile of radiant power striking the surface Measured in W/cm^2 or mW/cm^2. Higher peak irradiance has beneficial effect on cure speed and depth of cure.
2. Spectral distribution
Relative radiant power versus emission wavelengths measured in nm. Lamp spectral distribution and photoinitiator absorption must be matched for optimum curing
3. Exposure time
Energy is the time - integral of irradiance expressed as J/cm^2 or mJ/cm^2.
4. Infrared (IR)
Typically determined by the temperature rise of the substrate or by a non-contact thermometer

EB CURE REQUIREMENTS
Unlike in UV curing, the terminology used In EB curing for the effective energy is Dose. The absorbed dose of electron energy is calculated from the following equation:

$$D = K \times I/V$$

D = Megarads
K = Processor constant
I = Beam current in milliamps
V = Line speed in ft/min.

1 Megarad = 10 kGy (kilo gray)

Radiochromic film dosimeter can be used to determine the uniformity of dose across the width of the product being cured

When curing with EB, it is critical to operate at the voltage that is optimum for the density of the coating being cured. Too high a voltage will result in most of the electrons passing through the coating without effecting a cure. Too low a voltage will result in too few electrons penetrating the coating layer. The unit of measurement used for dose in EB curing is called a Megarad (Mrad). A typical power rating for a EB curing unit is 1,000 Mrad meter/minute. This means the EB unit delivers 1 Mrad at a line speed of 1,000 meter/minute. Decreasing the line speed by one-half doubles the applied dose. A typical dose used for EB curing is between 0.5 and 3.0 Mrads. It is important to use the minimum dose required to provide satisfactory film properties in EB curing as a higher dose may result in substrate degradation.

As with any other coating system, it is important to utilize a test method for determining when the UV/EB coating is fully cured. Several techniques, which can be used individually or in combination, are as follows:

- Measuring a functional property – for example, film modulus, film hardness, film adhesion and film gloss

- Using a chemical method – for example, spectroscopic measurement of residual unsaturation, solvent extractables, cured film volatiles, and cured film solvent sensitivity.

APPLICATIONS OF UV/EB COATINGS

Coatings for wood

UV/EB curable liquid coatings are used for various wood applications including: abrasion resistant flooring, assemble yourself furniture, sealers and basecoats, particleboard (EB), simulated woodgrain transfer laminates (EB), trim moldings, and baseboard. A vacuum application technique is used to apply the UV coatings to trim moldings and baseboard. Advantages of UV/EB coatings include fast line speed, excellent stain resistance, and durability.

Coatings for plastic

Coatings for web form plastic films

UV curable coatings are used for coating various plastic films including: polycarbonate, polyester, and polypropylene. These coatings are applied on a web line and offer line speed and performance advantages over conventional coatings. Applications include: solar control plastic films, appliance touch panel films and display films. In addition to fast line speed and absence of solvent, these coatings offer desirable cured film properties, such as print receptive films, varying cured film textures, and excellent resistance to stain and abrasion.

Coatings for CDs and DVDs

The rapid cure speed of UV curable coatings has enabled manufacturers of CDs and DVDs to maximize manufacturing line speed (~ 3 to 4 seconds per unit). Two different types of UV materials are used in the manufacture of CDs. First, a UV abrasion resistant clear coat is spin coated onto the metal reflective layer. The protected metallized surface is then screen printed with a UV curable ink. In the case of DVDs, a UV curable adhesive is used to bind the protective polycarbonate layer to the metallized polycarbonate layer. The viscosity of the CD clear coat varies between 10 to 100 cps at 25^{o} C, and the viscosity of DVD adhesives is less than 1,000 cps at 25^{o} C.

Electronics

Printed circuit boards are protected from harsh environmental conditions with a UV curable conformal coating. One of the challenges in developing a UV curable conformal coating is the irregular surface of the printed circuit board. The crevices and hidden areas created by the irregular surface make it impossible to achieve complete line-of-sight curing. Formulators have developed coatings that undergo post curing in areas that have not been directly exposed to UV light.

Coatings for 3-D substrates

Curing techniques have been developed for curing UV curable coatings applied to a three-dimensional substrate. The coating is applied either by spray application or vacuum deposition. The coated substrate, suspended on a conveyerized system, is then rotated in front of a series of UV lamps positioned to expose the entire coated surface to UV light. Applications include topcoats for wooden furniture and polycarbonate headlamps. Basecoat s and topcoats are used for vacuum metalized perfume lids, automotive headlight reflectors, plastic door handles, and plastic flowerpots. Another three-dimensional application is a base coat sealer used on SMC automotive fenders. One of the major advantages the UV curable sealer offers for vacuum metalized plastic parts is prevention of outgasing during the vacuum metalization process.

Adhesives

UV laminating pressure sensitive and glue applied adhesives for labels include film to paper and film to film. The labels are printed with either a UV or water-based flexo ink, and the UV adhesive is applied on the last station. This is followed by attachment of the film, and the film laminate is exposed to UV light for curing. This lamination technique has the advantage of being carried out in-line at a lower cost than using conventional adhesives. Advantages of UV/EB lamination include achieving full bond strength immediately upon cure, stabilizing the adhesive until cured, and eliminating viscosity adjustments.

Another type of UV curable adhesive in commercial use is the "assembly" adhesive. These adhesives are used in the manufacture of cell phones, medical devices such as catheters and syringes, automotive parts and optical fiber splices. These adhesives are typically dispensed with a syringe and cured with a "spot" curing device in-line. The advantage in using the UV curable adhesive is the rapid cure that allows the products to be completely assembled in-line. A fluorescent dye is commonly added to UV curable adhesives as an inspection aid to insure the adhesive flowed properly in the device.

Release coatings

Both UV and EB curable release coatings are in commercial use. Line speeds for these coatings run about 1,000 feet/minute. The UV release coating is based on cationic curing and can be processed in open air while the acrylate-free radical based systems must be cured in a nitrogen gas atmosphere. Release properties are competitive with non-UV/EB release coatings.

Metal application

Galvanized steel piping is protected with a UV curable coating applied in-line as the last step in the pipe manufacturing process. The coating provides protection against white rust while the pipe is stored outdoors. Originally, the coating was applied by a squeegee applicator. More recently, a vacuum technique has been developed to apply the coating.

Nameplate manufacturers have found UV curable coatings offer outstanding line speed and performance properties in coating metal stock. UV cured coating provides an eye appealing "glassy" look to metal nameplate, and the coated metal can be post formed even at a film thickness up to three mils. Special dome and lens look can be achieved with UV coatings up to 1/8th inch thick.

Many of the beverage companies use UV curable inks for decoration. Ink layers up to 0.5 mil can be cured with UV light at acceptable line speeds.

Coatings for optical fibers

UV curable coatings have been the choice coating technology for manufacturing optical fibers since fiber began to be used commercially in the late 1970s. A soft primary and tough secondary coating are applied in sequence as the glass fiber is drawn from the molten glass preform. Typically, UV lights are positioned immediately after the primary coating applicator and secondary coating applicator. However, some fiber is produced by a wet-on-wet coating process in which UV lights are positioned only after the secondary coating applicator. In the wet-on-wet process, both the primary and secondary coatings cure simultaneously. Line speeds exceeding 5,000 feet/minute are common in manufacturing optical fiber. UV curable inks are used to color code fiber in an off-line operation. Fibers used in and around the city are usually installed in a ribbon configuration in which several individual fibers are bound side by side. The matrix material used to bind the fibers together is also a UV curable coating.

UV/EB Inks and clear coatings for graphic arts

1. Offset lithography

UV/EB curable inks and coatings offer several options for offset printing. These include:

Process	Results/Benefits	Line Speed Range (ft./min.)
Print sheet fed stock by conventional air dry inks then apply UV clear coating off-line as second step after the ink has dried	• High gloss mar resistant finish	• 400 - 600
Print web stock with heat-set inks and apply UV clear coating in-line on last station	• High gloss, mar resistant finish	• 700 - 900

Print sheet fed stock with conventional air dry inks and replace spray powder/water based primer step with UV clear coating on last station	• Eliminates the need to dry ink • Reduces floor space requirements • Printed stock can be fabricated in-line • Coated stock has medium gloss mar resistant finish	• 600 - 700
Print web and sheet fed stock with UV inks and UV clear coating. (Hybrid ink being developed that is compatible with standard rubber rollers)	• Produces high gloss durable printed stock • Inks will not dry on printing rollers • Inks can be left on printing press overnight	• 400 - 800
Print stock with EB curable inks and clear coating	• Eliminates the need for inter-station curing with UV inks. • Inks and coating are cured in one step at the end of the line • Produces high gloss finish at high speeds	• 900 - 1,000 (limited to in-line die cutting operation)

2. Ink Jet

One of the major obstacles in commercializing UV/EB curable inkjet inks is the low viscosity requirement for inkjet printing. UV/EB curable formulations generally require a portion of high molecular weight oligomer to enhance cured film adhesion and toughness. These relatively high molecular weight materials significantly increase coating viscosity. Recent developments in print heads, based on Piezo technology, have expanded the viscosity range for inkjet printing to accommodate UV/EB curable inkjet inks. UV/EB curable inkjet inks are available at viscosities in the 10 to 50 cps range at 55^{o} C.

3. Flexo

UV and EB curable inks are available for flexo printing. Ink viscosities range from 300 to 500 cps. One of the advantages in printing with UV/EB curable inks is superior dot gain achieved with these inks over solvent-based flexo inks. Typical line speed for UV inks used on narrow web label lines is 500 to 600 feet/minute. Web trapping with EB curable inks eliminates the need to change solvent and can be run at line speeds varying between 1,000 to 1,500 feet/minute on film stock.

Powder coatings

UV powder coatings offer two major advantages over conventional powder coatings: 1) they do not cure during the melting step and (2) they melt at lower temperatures than conventional powder coatings. These two advantages enable post-curing operations to be done in-line with less space requirements and at faster speeds than a conventional powder coating line. Applied coating thickness can be controlled from 1.5 to 4.0 mils. Cured film properties include excellent solvent, salt spray, and stain resistance in addition to excellent substrate adhesion. Applications for UV curable powder coatings include metal, plastic (requires conductive primer/conductive additive) medium density fiberboard (MDF), electric motors, automobile radiator, PVC flooring, furniture, galvanized steel, and engine blocks. Three-dimensional applications are under development.

Solid Imaging

During the last 15 years, companies have been able to take advantage of using UV curable coating technology to dramatically reduce the time it takes to make complex prototype devices. This technique, often referred to as stereolithography, uses CAD information to generate a three-dimensional "build" file of the desired prototype. The build file consists of a stack of thin two-dimensional cross sectional layers that together duplicate the prototype. Software then uses this build file to direct a laser beam in a vat containing a photopolymerizable liquid. As the laser traces each layer of the prototype, a replica of each layer is formed as a polymerized layer in the vat. Each slice has a film thickness of between 0.001 to 0.020 inch. The polymerized layer rests on a build platform. The build platform is then lowered into the vat to a predetermined level and the polymerized layer is covered with fresh uncured coating. The laser then traces out the next cross sectional layer of the prototype and creates a new layer of polymerized coating on top of the first layer. This process of curing the top liquid layer and lowering the build platform is repeated until the prototype is duplicated as a hardened resin in the vat of liquid coating. At the end of the process, the build platform is raised. Then, the duplicated prototype is removed from the vat and undergoes additional processing. This method of making prototypes is measured in hours instead of weeks using the conventional method of making molds.

SAFE HANDLING OF UV/EB CURABLE COATINGS

In general, the acrylates used in UV/EB curable coatings are relatively safe when used as directed on the product MSDS. Moreover, solvent-free UV/EB curable coatings do not pose an inhalation problem under normal plant ventilation conditions.

Acrylates are considered to be skin irritants and skin sensitizers. Therefore, as with any other liquid chemical, it is important to prevent skin and eye contact when handling UV/EB curable coatings. Wearing chemical resistant gloves, safety glasses or goggles, and a work uniform or protective apron are required to safely handle UV/EB curable coatings. Clothing soiled with acrylates should be removed immediately to prevent skin contact. Washing hands routinely with lukewarm water and a mild soap is also advisable to remove any undetected acrylate that may have come with the skin. Depending upon the situation, wearing a plastic bootie over shoes may be advisable. The skin and eye irritation and sensitization hazards are eliminated once the coating is fully cured. Instructing employees in the safe handling of UV/EB curable coatings should be part of an employee-training program.

When storing acrylate-based coatings, it is important to insure the presence of air in the container. The oxygen in air helps to prevent the liquid coating from increasing in viscosity. Contamination with water, acid and base should be avoided when storing cationic curable formulations. It is also advisable to check the supplier's MSDS for proper storage temperature conditions. In general, UV/EB curable coatings should be stored between 60^{o} and 80^{o} F.

Avoid using high shear pumps (piston and gear) when transferring UV/EB curable coatings. The two recommended types of pumps for transferring UV/EB curable materials are a diaphragm and peristaltic pump.

LEGAL AND REGULATORY CONSIDERATIONS

All products used commercially must be compliant with national chemical inventories. In the United States, all components in a commercially used product must be listed on the TSCA Chemical Inventory. Other countries have their version of TSCA that must be followed. If you are a coating supplier, it is important to make sure you are not manufacturing or selling your product in a country in which the product infringes a valid patent. If you own a patent for a product you are selling, you should consider implementing a patent-marking program to maximize the effectiveness of your patent. If you are an end user of a product, you should check to make sure you are not infringing a valid patent.

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